



Arsenic in volcanic geothermal fluids of Latin America

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ABSTRACT

Numerous volcanoes, hot springs, fumaroles, and geothermal wells occur in the Pacific region of Latin America. These systems are characterized by high As concentrations and other typical geothermal elements such as Li and B. This paper presents a review of the available data on As concentrations in geothermal systems and their surficial discharges and As data on volcanic gases of Latin America. Data for geothermal systems in Mexico, Guatemala, Honduras, El Salvador, Nicaragua, Costa Rica, Ecuador, Bolivia, and Chile are presented. Two sources of As can be recognized in the investigated sites: Arsenic partitioned into volcanic gases and emitted in plumes and fumaroles, and arsenic in rocks of volcanic edifices that are leached by groundwaters enriched in volcanic gases. Water containing the most elevated concentrations of As are mature Na–Cl fluids with relatively low sulfate content and As concentrations reaching up to 73.6 mg L⁻¹ (Los Humeros geothermal field in Mexico), but more commonly ranging from a few mg L⁻¹ to tens of mg L⁻¹. Fluids derived from Na–Cl enriched waters formed through evaporation and condensation at shallower depths have As levels of only a few µg L⁻¹. Mixing of Na–Cl waters with shallower meteoric waters results in low to intermediate As concentrations (up to a few mg L⁻¹). After the waters are discharged at the ground surface, As(III) oxidizes to As(V) and attenuation of As concentration can occur due to sorption and co-precipitation processes with iron minerals and organic matter present in sediments. Understanding the mechanisms of As enrichment in geothermal waters and their fate upon mixing with shallower groundwater and surface waters is important for the protection of water resources in Latin America.

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1. Introduction

In Latin America, volcanism and geothermal systems are more common in the Pacific zone (Fig. 1), which is an intensively populated region with a high demand of potable water. The presence of As in geothermal waters and its environmental impact has long been recognized, e.g. Long Valle Caldera, USA (Wilkie and Hering, 1998); Los Azufres, Mexico (Birkle, 1998; Birkle and Merkel, 2000); Los Humeros, Mexico (González et al., 2001). The purpose of this paper

is to present a general overview of the state of As contamination arising from geothermal resources in Latin America, and to identify processes that produce high As concentrations and mechanisms that immobilize or release As into the environment.

Geothermal activities are associated with four different settings (Chandrasekharam and Bundschuh, 2002): active volcanoes, continental collision zones, continental rift systems associated with active volcanism, and continental rifts not associated with volcanoes. In the case of Latin America, As-rich geothermal waters are usually associated with areas of active volcanism. Birkle and Bundschuh (2007b) have identified the mixing of As-rich geothermal groundwater with cold aquifers as the main environmental problem in As contamination. However, in some cases, As-rich surface waters are found in rivers and lakes close to spring discharges (e.g. Cumbal et al., 2009), or in lakes filling volcanic calderas (e.g. López et al., 2009).

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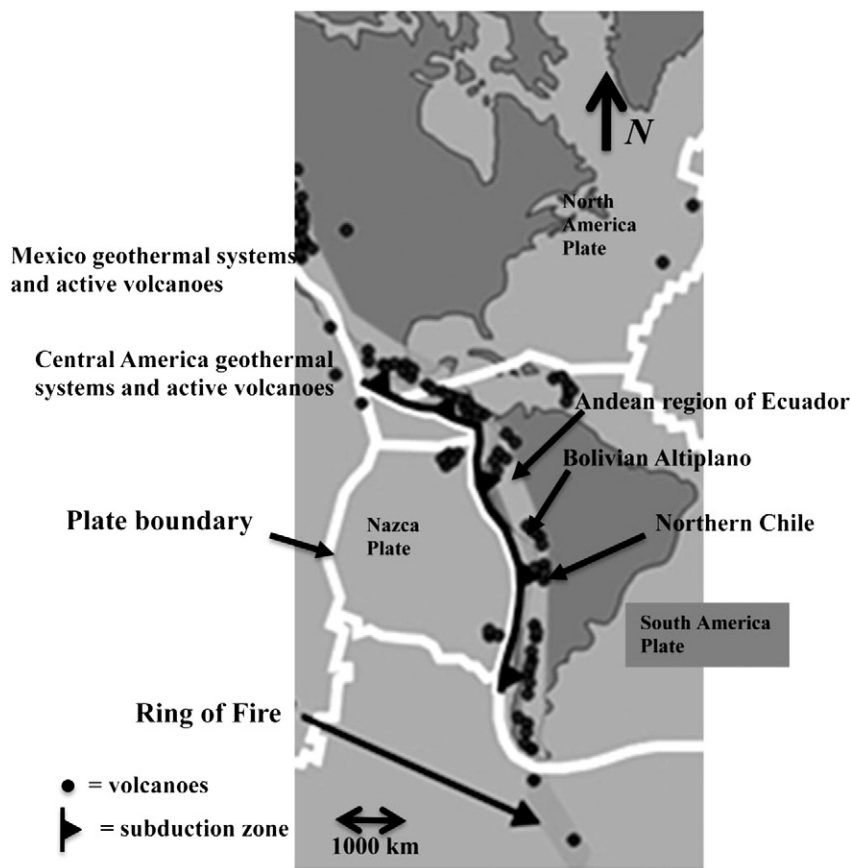


Fig. 1. Location map showing volcanoes, the ring of fire, and plate boundaries.

Even when As is detected in some volcanic emissions (e.g. Signorelli, 1997), it is not common to find reports of As concentrations for volcanic gases (e.g. Gemmel, 1987; Mambo and Yoshida, 1993). The way that As is partitioned between the volcanic fluids and the magma is not well understood due to lack of data in the melt and gas phase. Experimental and theoretical work on the stoichiometry and stability of As gaseous complexes in the system As–H₂O–NaCl–H₂S at temperatures up to 500 °C and pressures up to 6×10^7 Pa (600 bars, Pokrovski et al., 2002b) indicate that As(OH)₃(gas) is the predominant As complex in both volcanic gases and boiling hydrothermal systems. This species is proposed as responsible for the preferential partitioning of As into the vapor phase as observed in fluid inclusions from high-temperature magmatic-hydrothermal ore deposits (Pokrovski et al., 2002b).

With respect to As in fumarole gases, studies in Yellowstone (USA) show that toxic inorganic AsH₃ is the most volatile of the inorganic species. Organic methylated species (CH₃)₂AsCl is the most commonly found in the gas phase, followed by (CH₃)₃As, (CH₃)₂AsSCH₃, and CH₃AsCl₂ (Planer-Friedrich et al., 2006). The degree of toxicity of the methylated forms is unknown.

In comparison, the behavior of sources and fate of As in geothermal systems are better understood (e.g. Arellano et al., 2003; Birkle and Bundschuh, 2007b; Goff et al., 1986a; González et al., 2001). In deep geothermal systems, reducing conditions prevail. Arsenic is present as As(III) and the solution is undersaturated with respect to arsenopyrite and other As minerals (Webster and Nordstrom, 2003). These undersaturated conditions also occur for minerals containing B, F, Li, Hg, Se, and Tl. According to Webster and Nordstrom (2003), arsenopyrite is not a conspicuous mineral in geothermal systems. Birkle et al. (2010) state that the saturation state of geothermal waters with respect to arsenopyrite depends on reservoir temperature.

For temperatures between 150 and 250 °C, As occurs as As-bearing pyrite rather than as arsenopyrite, or is associated with iron oxides. At higher temperatures, arsenopyrite (FeAsS) and other As-bearing minerals can be found. Equilibrium between As-bearing pyrite and fluids is responsible for the As concentrations measured in high and moderate temperature hydrothermal systems, with local dissolution of arsenopyrite creating more reducing conditions which are likely to favor the precipitation of gold from hydrothermal solutions (Pokrovski et al., 2002a, 2002b).

Arsenic can be present in geothermal reservoirs as well as in spring discharge and fumarolic gases. However, the highest concentrations of As are found in mature NaCl waters (up to tens of thousands µg/kg) that have been in contact with the rocks for a long period of time (Birkle et al., 2010), suggesting that the increase in As concentration is due to the longer residence time (and leaching) of the waters. Thus, As concentrations are considerably higher in geothermal systems occurring in volcanic rocks than in high and low enthalpy systems in sedimentary rocks. The path of geothermal reservoir waters to the surface can occur in four different ways. (1) If the upflow (for example along a fault zone to the surface) is fast, with a minimal loss of conductive heat to the wallrock, the composition of the discharging water is similar to the reservoir water producing a Na–Cl rich water, with near neutral pH, high silica content due to the long rock–fluid interaction, sulfate concentrations lower than Cl concentrations, and enrichment in CO₂ and H₂S gases. These are the mature Na–Cl waters described by Giggenbach (1988). Consequently, these waters should present As concentrations close to reservoir concentrations. (2) If a vapor phase rich in H₂S separates from the reservoir due to pressure changes, and the vapor condenses at shallower levels, acid sulfate waters low in Cl are formed (Giggenbach, 1988). According to Birkle et al. (2010), these condensed waters are low in As because As is partitioned

preferentially into the reservoir water instead of the vapor phase, leaving water enriched in As in the lower evaporated aquifer. (3) If the upflow of Na–Cl waters occurs in such a way that the waters have time to oxidize, H_2S is oxidized to sulfate (and different species of sulfate in solution such as HSO_4^-) and the pH of the water decreases. These are the acid sulfate–Cl waters described by Giggenbach (1988) in volcanic settings. As the As-rich waters ascend and get close to the atmosphere, oxygen-rich waters can mix with the geothermal waters, or soil air in the unsaturated zone, promoting the conversion of As(III) to As(V) and precipitation of As minerals if the concentrations are high enough. (4) Mixing of Na–Cl waters with shallower meteoric waters can produce the bicarbonate-rich waters described by Giggenbach (1988).

After reviewing published fluid analyses from geothermal systems, Ballantyne and Moore (1988) concluded that As concentration of reservoir fluids varies inversely with $P_{\text{H}_2\text{S}}$ and increases with temperature. When vapor separation occurs in geothermal waters, As and Cl remain in the liquid phase producing a significant positive correlation between these two elements (Webster and Nordstrom, 2003). Arsenic concentrations in Na–Cl waters can reach high values, e.g. 50 mg L^{-1} in El Tatio geothermal field in Antofagasta, Chile (Ellis and Mahon, 1977; Smedley and Kinniburgh, 2002). In comparison, As concentrations in acid sulfate-dominated waters are usually in the lower tens of mg L^{-1} (Planer-Friedrich et al., 2006).

Once the waters, or gases from fumaroles, reach the atmosphere, the oxidation of As(III) occurs along the path of the fluid, converting it to As(V). Arsenic (III) can still be present in the water under oxidizing conditions in areas of the discharge zone close to hot springs if the oxidation kinetics is slow. However, the As oxidation process in the surface waters can be accelerated by the presence of bacteria attached to submerged macrophytes, as observed in stream waters of the eastern Sierra Nevada (Wilkie and Hering, 1998).

In the following sections, selected geothermal sites in Latin America with significant As concentrations are presented. It is not possible to include all sites because many have not been investigated thoroughly and, for others, the data are not public. The chemical characteristics of the different geothermal waters and their As concentrations will be compared to understand their evolution from the source to the discharging point and in the surface environment. In Table 1, data are divided by country, studied site, type of discharge, and, when possible, water type. Standard deviations are not reported because most sites only have a small number of samples and the statistical distribution is unknown. A complete data set for the concentrations and field parameters used in this study, including descriptive statistics and references, is in the Supplemental Table on the journal website.

2. México

Favorable geologic–tectonic conditions explain the widespread distribution and abundance of hydrothermal systems and active volcanoes in México. Especially within the Transmexican Volcanic Belt (TMVB), dominant vertical pathways of fracture and fault systems allow the convective circulation of geothermal fluids. Subduction of the Rivera and Cocos plates under the North American and Caribbean plates produces thousands of volcanic structures; the majority are located within two major arcs: the 1200-km long TMVB and the northwest-trending, Sierra Madre Occidental volcanic province (SMO). More than 2300 geothermal localities with low- to medium-temperature conditions (28–200 °C) are identified in 27 of 32 Mexican states (Birkle, 2007; Martínez-Estrella et al., 2005; Torres et al., 1993, 2005), most being concentrated within the roughly east–west trending TMVB in central Mexico (Fig. 2). Of 1380 studied manifestations, there are 808 warm–hot thermal springs, 526 hot wells, 25 fumaroles, 6 mud volcanoes, 11 bubbling springs, and 3 hot soils. There are 68 high enthalpy sites with temperatures above 150 °C (Herrera and Rocha, 1988). Unfortunately, analytical data on the composition of thermal springs, crater lakes, and groundwater in Mexico, including As concentrations, are limited.

In this section we present a summary of available data on As concentrations in waters influenced by volcanic activity, thermal fluids from surface manifestations, and deep geothermal reservoirs in Mexico.

2.1. Mexican geothermal systems

The range of As concentrations for Mexican geothermal fluids can be found in Table 1. A detailed listing and interpretation of As data from both, geothermal, and petroleum reservoirs in Mexico are reported in Birkle and Bundschuh (2009) and Birkle et al. (2010).

2.1.1. Cerro Prieto geothermal field

The Cerro Prieto geothermal field (Fig. 2) in northern Baja California is hosted in deltaic sandstone and shales of the southern Salton Sea. Geothermal fluids are sourced from depths between 800 and 3000 m with an average reservoir thickness of 1900 m. An igneous intrusion, emplaced at a depth of 5–6 km, supplies heat to the Cerro Prieto system (Elders et al., 1984), with reservoir temperatures above 260 °C. Arsenic data were compiled from Mercado et al. (1989) and Lippman et al. (1999) for chemical data on Cerro Prieto fluids, and Portugal et al. (2000b) and Mazor and Mañón (1979) for chemical and stable isotope composition of geothermal fluids. The dominance of sandstones in the sedimentary basin of the Cerro Prieto geothermal field explains the relatively low As concentrations of 0.25 to 1.5 mg L^{-1} (Table 1) in reservoir fluids.

2.1.2. Las Tres Vírgenes geothermal field

The Las Tres Vírgenes (LTV) geothermal field is located in the middle of the Baja California peninsula. Since 1988, nine wells have been drilled to a maximum depth of 2420 m (López, 1998). A post-Cretaceous granodioritic intrusion and the volcano-sedimentary Grupo Comondú form the major hydrogeologic reservoir units of the geothermal system (Portugal et al., 2000a). Fluid compositional data and reservoir temperatures from three production wells at this geothermal field are reported by Portugal et al. (2000a) and Viggiano-Guerra et al. (2009). Arsenic concentrations between 6.5 and 6.7 mg L^{-1} for LTV geothermal water (Birkle et al., 2010) are probably related to the dissolution of As from traces of primary As minerals or from dispersed As inclusions in the granodioritic basement. No primary As minerals (Quijano-León and Gutiérrez-Negrín, 2003) have been documented for the LTV reservoir.

2.1.3. Los Azufres geothermal field

Los Azufres is one of several Pleistocene silicic volcanic centers, with active geothermal systems in the E–W trending TMVB, providing vapor and liquids from a depth between 350 and 2500 m. A 2700 m thick interbedding of lava flows and pyroclastic rocks of andesitic to basaltic composition (Dobson and Mahood, 1985) provides the main aquifer with fluid flow through fractures and faults that sometimes reach the surface (Birkle et al., 2001). The NaCl-rich fluids reach maximum temperatures of 320 °C, but temperatures of 240–280 °C are common. González et al. (2000) and Birkle (1998) present analytical results from 17 deep wells with As concentrations between 5.1 and 28.4 mg L^{-1} .

2.1.4. Los Humeros geothermal field

This geothermal field is located in the eastern part of the TMVB, with a total of 42 wells of which 22 are currently used for electricity generation. Metamorphosed carbonate forms the basement below a low-liquid-saturation reservoir, which is located at a depth between 1950 and 2700 m (850–100 m a.s.l.). Basalt and hornblende andesites of intermediate permeability form the host rock of the deeper reservoir, whereas augite andesite hosts the upper geothermal reservoir (800–1700 m) (Arellano et al., 2001; Cedillo, 1999). Major and minor elemental compositions of 24 fluid samples from this geothermal field are reported by González et al. (2001) and Arellano et al. (2001). The chemical variability in the Los Humeros reservoir (Table 1) can be explained

Table 1
 Arsenic concentrations, temperature, pH, and TDS for geothermal waters of Latin America. Concentrations and TDS in mg L⁻¹. Alkalinity in mg L⁻¹ of CaCO₃. For Costa Rican waters, asterisk indicates Electrical conductivity (EC) in $\mu\text{S cm}^{-1}$.

Site	N	Discharge type	Water type	Mean Temp (°C)	Max. Temp (°C)	Min. Temp (°C)	Mean pH	Max pH	Min pH	Mean TDS or EC	Max TDS or EC	Min TDS or EC	Mean As total	Max As total	Min As total
<i>Mexico</i>															
Cerro Prieto GF	3	Well	Na–Cl	300	300	300	8.0	8.0	8.0	28,200	40,150	16,450	0.88	1.50	0.25
Las Tres Virgenes GF	2	Well	Na–Cl	245	250	245	7.4	7.4	7.4	3550	3990	3110	6.60	6.70	6.50
Los Azufres GF	14	Well	Na–Cl	275	329	202	7.3	7.9	6.5	7551	11,040	5410	24.00	29.50	5.10
Los Humeros GF	17	Well	Na–Cl to Na–HCO ₃ –SO ₄ –Cl	304	330	280	7.7	8.7	6.6	2419	2740	1070	21.00	73.60	1.90
El Chichón volc.	1	Spring	Na–Cl	58			2.2						0.15		
El Chichón volc.	1	Crater lake	Na–Ca–Cl–SO ₄	36			2.3						0.17		
Colima volc.	1	VGC		828									0.53		
Popocatepetl volc.	1	Crater lake	Mg–SO ₄ –Cl	21			1.5						1.20		
Popocatepetl volc.	2	Spring	Ca–Mg–HCO ₃ –SO ₄ , Mg–Ca–Na–HCO ₃ –SO ₄	21	26	17	6.7	6.7	6.7	533	964	101	0.04	0.05	0.03
<i>Guatemala</i>															
Tecuamburro GF	1	Hot spring	Ca–Mg–SO ₄	77			2.5						0.10		
Tecuamburro GF	3	Hot spring	Na–Cl to Na–HCO ₃ –Cl	59	96	39	6.5	7.0	6.0				0.80	2.00	0.10
Zunil GF	2	Hot spring	Na–HCO ₃ –Cl Mg–Ca–Cl–SO ₄	68	74	61	7.5	7.6	7.4	1177	1683	670	0.31	0.34	0.27
Zunil GF	8	Well	Na–Cl	239	278	95	7.4	8.4	5.7	2826	4222	212	4.83	12.34	0.14
Moyuta GF	2	Hot spring	Na–HCO ₃ –Cl–SO ₄	71	75	67	7.2	7.2	7.2				5.75	6.60	4.90
<i>Honduras</i>															
Azacualpa GF	1	Hot spring		115									0.07		
Pavana GF	1	Hot spring		102									0.11		
Platanares GF	15	Hot spring	Na–HCO ₃ –SO ₄	98	100	95	8.7	9.1	8.0				0.94	1.26	0.68
<i>El Salvador</i>															
Ahuachapan GF	7	Cold spring	Ca–Mg–HCO ₃ –SO ₄ to Mg–Na–Ca–HCO ₃	29	32	19	6.6	7.0	6.1				0.04	0.09	0.01
Ahuachapan GF	1	Hot spring	Ca–Na–SO ₄	76			7.3						0.01		
Ahuachapan GF	1	Crater Lake	Mg–Ca–HCO ₃	19			6.4						0.21		
Ahuachapan GF	3	Domestic well	Na–Mg–Ca–HCO ₃ , Na–HCO ₃ –Cl	32	33	30	6.9	7.5	6.6				0.08	0.09	0.08
Coatepeque C.	2	Hot spring	Na–Cl	66			6.7						2.3	3.1	1.5
Coatepeque C.	7	Lake water	Na–Cl–SO ₄	24			8.5						0.80	0.50	1.19
Ilopango C.	12	Lake water	Na–KHCO ₃ –Cl										0.53	0.78	0.15
Berlin GF	6	Hot spring	HCO ₃ , HCO ₃ –SO ₄	58	96	38	6.7	7.6	5.3				0.04	0.16	0.01
Berlin GF	1	Hot spring	Cl	101			8.1						0.33		
Berlin GF	5	Well	Na–Cl	6.4	7.0	6.1	11.7	16.7	7.8						
<i>Nicaragua</i>															
Monte Galan	3	Hot spring	Na–HCO ₃ –SO ₄ to Na–Mg–Ca–HCO ₃ –SO ₄ –Cl	44	47	41	6.6	6.8	6.4	1126	1220	970	0.11	0.12	0.11
Momotombo GF	3	Well	Na–Cl	80	100	39	8.3	8.4	8.1	4932	7026	3853	2.09	2.65	1.74
Cerro Negro volc.	7	VGC	Mg–Cl to Ca–Mg–Cl–SO ₄	263	315	170	1.5	2.0	1.2				0.07	0.10	0.03
Masaya volc.	3	VGC	Na–Cl to KCa–SO ₄ –Cl	112	150	85	3.7	4.4	2.7				0.16	0.40	0.04
Telica volc.	1	VGC	K–Cl	150			2.6						0.08		
Momotombo volc.	5	VGC	Na–Mg–Cl to Na–Mg–Cl–SO ₄	532	666	471	0.8	0.9	0.7				0.30	0.49	0.23
<i>Costa Rica</i>															
Miravalles GF	13	Well	Na–Cl	234	242	227	7.0	7.8	4.8	12,728*	15,150*	8940*	25.42	29.13	11.86
Miravalles GF	11	Hot spring	Na–HCO ₃ to Mg–Ca–HCO ₃ –SO ₄	47	89	34	4.9	7.3	2.0	1536*	4840*	260*	0.57	4.56	0.01
Miravalles GF	4	Cold spring	Ca–HCO ₃ –SO ₄ to Ca–Mg–HCO ₃	21	24	14	6.8	7.2	6.6	228*	300*	140*	0.01	0.01	0.01

Table 1 (continued)

Site	N	Discharge type	Water type	Mean Temp (°C)	Max. Temp (°C)	Min. Temp (°C)	Mean pH	Max pH	Min pH	Mean TDS or EC	Max TDS or EC	Min TDS or EC	Mean As total	Max As total	Min As total
<i>Costa Rica</i>															
Rincón de la Vieja GF	4	Well	Na–Cl	247	276	229	6.5	7.8	5.7	10,240*	12,850*	8000*	9.90	13.00	5.99
Rincón de la Vieja GF	8	Hot spring	Mg–Cl–SO ₄ to Ca–Mg–SO ₄ –HCO ₃	47	91	26	5.6	7.6	2.2	2122*	5850*	190*	0.02	0.05	0.01
Rincón de la Vieja GF	2	Hot spring	Na–Cl	71	71	71	6.1	6.1	6.1	9520*	9580*	9460*	10.74	10.85	10.63
Rincón de la Vieja GF	2	Cold spring	NaCl to Ca–Mg–SO ₄ –HCO ₃	27	27	27	6.9	7.8	6.0	295*	380*	210*	0.07	0.13	0.01
Poas volcano	2	VGC											8.6	14.7	2.6
Irazú volc.	1	VGC													0.013
Rincón de la Vieja volc.	1	VGC													0.05
Hornillas Miravalles volc.	1	VGC													0.05
<i>Ecuador</i>															
El Carchi	4	Hot spring	Cl to Cl–HCO ₃	39	54	31	6.2	7.3	4.8	581			0.277	0.684	0.002
Imbabura	4	Hot spring	Cl–HCO ₃	41	44	39	7.3	8.0	6.5	3187	3700	2710	0.683	0.974	0.004
Pichincha	7	Hot spring	HCO ₃ –Cl	35	42	29	6.8	7.4	6.3	1229	2310	412	0.184	0.405	0.048
Cotopaxi	3	Hot spring	HCO ₃ –Cl	24	34	19	6.5	6.7	6.4				0.032	0.045	0.012
Tungurahua	5	Hot spring	HCO ₃ –Cl, Cl	41	54	28	7.3	8.3	6.4				0.049	0.114	0.004
Papallacta Basin	7	Hot spring		41	63	14	7.0	8.2	6.2	1759	3500	162	4.19	7.85	1.09
<i>Bolivia</i>															
Poopo's Lake Basin	16	Hot spring	Na–Cl to Na–HCO ₃ –Cl	56	75	40	7.0	8.3	6.3				0.023	0.065	0.008
Coipasa a Uyuni	1	Cold spring	Na–Ca–SO ₄ –Cl–HCO ₃	17			8.3			622			0.03		
<i>Chile</i>															
Caritaya river	3	River	Cl				8.1	8.1	8.1	2287	3127	1620	2.66	3.20	2.26
Amuyo's lakes	3	Lake	Cl				6.9	6.9	6.8	11476	12481	10780	10.96	12.69	9.58
El Tatio	1	Geyser	Na–Cl	87			7.2			2630			7.60		
El Tatio	2	Hot spring	Na–Cl	87			6.3	6.4	6.2	9590			28.5	30.1	27.0
El Tatio	1	River	Na–Cl	22			7.7			6620			21.00		

by vertical groundwater zoning, with lower concentrations of As fluids (3.9–7.9 mg L^{−1}) in the liquid-dominated shallow part of the reservoir (1330–1755 m b.s.l.), but the highest and most heterogeneous As concentrations (1.9–73.6 mg L^{−1}) in the deeper (1985–3060 m b.s.l.), two-phase reservoir zone.

2.2. Mexican active volcanoes

Although eruptions of 15 volcanoes (11 polygenetic and 3 monogenetic) have been reported in historical times in México (De la Cruz-Reyna, 2001), As concentrations have mainly been determined in gases and waters influenced by the activities of only three volcanoes: Popocatepetl, El Chichón, and Colima.

2.2.1. Popocatepetl volcano

Popocatepetl is an andesitic–dacitic stratovolcano 5454-m-high located in the TMVB about 70 km southeast of Mexico City (Fig. 2). It has an elliptical summit crater, which contained a roughly circular lake (SEAN, 1986) that disappeared in 1994 before the onset of current activity (Armienta, 2008). Hydrogeochemical studies on the lake and springs discharging around or at the volcanic edifice (Armienta et al., 2000, 2008a, 2008b; Inguaggiato et al., 2005; Segovia et al., 2003) have not been focused on As, resulting in little concentration data.

In 1863, Lefort reported the presence of As traces in the crater lake waters of Popocatepetl (Clarke, 1911). Samples collected in February 1994 before the disappearance of the most recent lake contained 1.2 mg L^{−1} of As (Werner et al., 1997). Arsenic ranged from <0.001 to 0.053 mg L^{−1} in spring samples collected in 1994 and 1995 at various distances from the Popocatepetl summit (mean = 0.021 mg L^{−1}, n = 91) with the highest As concentrations furthest from the volcano (about 46 km south); two samples had also the highest temperature and Cl concentrations (Werner et al., 1997). Segovia et al. (2002, 2003) reported low As concentrations (from 0.001 to 0.003 mg L^{−1}, with mean equal to 0.002 mg L^{−1}, n = 6) in springs discharging from the volcano flanks. Low As concentrations were also measured in aqueous leachates of tephra erupted in 1996, 1997 and 1998. Up to 0.08 mg kg^{−1} were obtained, with a mean equal to 0.019 mg/kg, n = 17 samples (Armienta et al., 2002). Alkaline traps installed to collect gases in 1994 showed a pulse of As in the first months of that year (with a concentration rate up to 0.02 mg kg^{−1} day^{−1}) (Werner et al., 1997). The SO₂ emissions measured by COSPEC (Werner et al., 1997) was estimated as an average As flux of 0.10 t day^{−1}.

2.2.2. El Chichón volcano

This is an isolated volcano located 1100 m a.s.l. at the NW end of the Chiapas Volcanic Arc (CVA) (Fig. 2). The basement rocks are Cretaceous



Fig. 2. Location of potential hydrothermal sites (black dots), geothermal fields, and described volcanic sites on Mexican territory (modified after Birkle, 2007).

evaporites and limestones, with interbeds of epiclastic early Cenozoic sandstones and limestones (Canul and Rocha, 1981). The volcanic structures and deposits are calcalkaline in composition with a medium to high content of potassium. El Chichón produced eleven major eruptions in the last 8000 years (Espindola et al., 2000; Mora et al., 2007). Composition of the crater lake water has been studied since 1983 by various researchers (Armienta and De la Cruz-Reyna, 1995; Armienta et al., 2000, 2008a; Casadevall et al., 1984; Rouwet et al., 2008; Taran et al., 1998, 2008; Tassi et al., 2003). However, only some of the publications report As concentrations. Varekamp et al. (1984) measured up to 120 mg kg^{-1} (mean = 49 mg kg^{-1} , $n = 11$) in aqueous ash-leachates from the 1982 eruption. Variable As concentrations (from 0.032 to 0.17 mg kg^{-1}) were determined in water samples from the crater lake collected at various dates. Springs flowing from its flanks contained a wide range in As concentrations (from 0.01 to 0.146 mg L^{-1}), with a mean of 0.044 mg L^{-1} ($n = 7$). The highest concentration corresponded to an acidic ($\text{pH} = 2.18$) highly-saline ($\text{TDS} > 15,000 \text{ mg kg}^{-1}$), Na–Ca–Cl-type spring apparently influenced by a magmatic source with contribution from a deep brine (Armienta, 2008; Taran et al., 2008).

2.2.3. Colima volcano

Colima volcano, located in the western portion of the TMVB (Fig. 1), is an andesitic stratovolcano rising nearly 4000 m a.s.l. With a historical record of 25 eruptions since 1560, it is the most active volcano in Mexico (De la Cruz-Reyna, 1993). Chemical studies of fluids from fumaroles, lakes, rivers, and springs related with the activity of the volcano have been performed for about fifteen years (Armienta and De la Cruz-Reyna, 1995; Connor et al., 1993; Taran et al., 2000; 2001). Nevertheless, only data on As concentrations from gas emissions are available. Condensates

collected at Colima volcano in 1997 contained up to 0.525 mg kg^{-1} As (mean = 0.439 mg kg^{-1} , $n = 3$).

3. Central America

Volcanic- and tectonic-related hydrothermal systems are common in Central America because of the effects of two plate boundaries: the Motagua–Polochic transform faults that define the boundary between the North American and the Caribbean Plates and the subduction zone defining the boundary between the Cocos and Caribbean Plates (Fig. 3). Acharya (1983) suggested, as seen in Central America, that geothermal systems in the circum-Pacific rim are situated near the ends of plate boundary segments or in transverse zones that divide plates in blocks that have a length between 100 and 1000 km, corresponding to lateral breaks of the underthrusting plates. Fig. 3 shows the main geothermal systems in Central America. Location, lithology, local production history, and conceptual hydrogeologic model of the main geothermal sites in Central America are given in Birkle and Bundschuh (2007a), and the corresponding chemical and isotopic fluid composition in Birkle and Bundschuh (2007b). Arsenic concentrations in geothermal systems have been determined only in a few geothermal systems of the region (e.g. Platanares, Goff et al., 1986a; Zunil, Adams et al., 1991; Berlin, Jasmin et al., 2005). Selected geothermal systems with As data are discussed next.

3.1. Guatemala

Thirteen geothermal areas of interest have been investigated in Guatemala (Lima Lobato et al., 2003) (Fig. 3). Two geothermal systems are in exploitation, Zunil and Amatitlan with 28 MWe and 30



Fig. 3. Geothermal fields and volcanoes of Central America.

MWe proven capacity, respectively. The geothermal systems of Tecuamburro (Goff et al., 1989), Zunil (Adams et al., 1991), and Moyuta (Goff et al., 1991) contain As concentrations in the discharge waters.

3.1.1. Tecuamburro geothermal field

Tecuamburro geothermal field located in western Guatemala is related to the volcano with the same name (Fig. 3). Tecuamburro is a composite andesitic volcano of Pleistocene age (Duffield et al., 1992) that has an abandoned sulfur mine in the summit area and an acidic lake

0.5 km in diameter (Laguna Ixpaco) in its crater. Acid sulfate waters occur at Laguna Ixpaco, steam-condensate waters occur north of the volcano, and neutral Cl waters discharge at springs close to Rio Los Esclavos at the east side of the volcano (Goff et al., 1989). Some cold springs reflecting shallow circulation are also identified in the area. Arsenic concentrations are low ($<0.05 \text{ mg L}^{-1}$) in the cold springs, steam-condensate springs, and in the acid sulfate waters. Only Laguna Ixpaco has As concentrations slightly higher (0.10 mg L^{-1}). In comparison, the neutral Cl springs exhibit As concentrations ranging from 0.1 to 2.0 mg L^{-1} , with a mean of 0.8 mg L^{-1} ($n=3$; Goff et al., 1989).

3.1.2. Zunil geothermal field

Zunil geothermal field is located within the volcanic complex formed by Santa Maria, Cerro Quemado, and Zunil volcanoes, about 120 km to the west of Guatemala City. The area falls within a proposed caldera ranging in age from Tertiary to Pleistocene (Foley et al., 1990) with the caldera wall and related faults transferring the fluids and heat (Bennati et al., 2011). Only two of sixteen fumaroles and warm and hot springs sampled show detectable As concentrations (0.27 and 0.34 mg L^{-1}) and they correspond to two hot springs with higher concentrations of bicarbonate (665 and 210 mg/L , respectively, Adams et al., 1991). In comparison, the majority of the geothermal wells (8 out of 12 sampled wells) have high concentrations of As, ranging from 0.14 to 12.34 mg L^{-1} (mean = 4.83 mg L^{-1}), while pH ranges from 5.7 to 8.4 . Cold springs display no detectable As levels.

3.1.3. Moyuta geothermal field

This volcano lies in a west-trending belt of domes and lava flows of andesitic–dacitic composition overlapping the southern boundary of the Jalpatagua Graben (Williams et al., 1964) in eastern Guatemala, close to the El Salvador–Guatemala border. Chemistry of the thermal and non-thermal waters allows the identification of four different types of waters (Goff et al., 1991): a) dilute Ca–bicarbonate non-thermal cold springs, b) fumaroles and steam-heated bicarbonate-rich springs at the north and south flanks, and c) acidic sulfate-rich springs in the fumarole areas, where the As concentration is below the detection limit; and d) Cl-rich springs that occur at the lower elevations along rivers and have pH ranging from 6.5 to 7.2 . As concentrations, as well as F, B, and Li, are detected only in two of four springs sampled (4.9 and 6.6 mg L^{-1}).

3.2. Honduras

Honduras has only a relatively short boundary with the Pacific Ocean (and the Cocos–Pacific plate boundary) at the Fonseca Gulf. However, due to the presence of several grabens and extensional faults, Honduras has a large number of thermal sites. Finch (1987) mentioned the existence of 125 thermal springs (temperature $>30^\circ\text{C}$) and 56 additional sites that have not been verified. Goff et al. (1986b) studied the geochemistry of springs in six geothermal sites in Honduras and detected As in three of them – Azacualpa, Pavana, and Platanares (Fig. 3) – with As concentrations of 0.07 , 0.11 , and 1.26 mg L^{-1} , respectively, based on one sample from each site. Arsenic was not detected in the other three sites (El Olivar, Sambo Creek, and San Ignacio (Fig. 3)). More extensive geochemical work has been done at three sites: Platanares, La Tembladera, and Azacualpa geothermal systems (Aldrich et al., 1987; Eppler et al., 1987; Laughlin, 1988), but As concentrations were reported only from the Platanares geothermal field.

3.2.1. Platanares geothermal field

This geothermal field is located about 16 km west of the city of Santa Rosa de Copán in west-central Honduras. Silicic tuffs and andesite lava flows are underlain by red beds of Cretaceous age (Laughlin, 1988). Waters discharge in many hot springs of alkaline–Cl composition, which have equilibrated at greater depths with sedimentary rocks at temperatures of 200 – 245°C as indicated by chemical and isotopic geothermometers (Birkle and Bundschuh, 2007b; Janik et al., 1991). A conceptual model of a high temperature fluid ascending through faults and cooling by conduction to form a 160 – 165°C shallow reservoir has been proposed (Janik et al., 1991). Hot springs may be sourced from boiling and steam loss of the parental fluid. Goff et al. (1986a) and Janik et al. (1991) studied the hydrogeochemistry and divided the waters into three types: end-member geothermal waters, cold waters, and mixed geothermal waters. Arsenic was not detected in the cold waters, in the geothermal waters, As concentrations ranged from 0.68 to 1.26 mg L^{-1} (mean = 0.94 mg L^{-1} , $n = 15$), with pH values of 8.0 to 9.0 .

3.3. El Salvador

El Salvador is characterized by numerous volcanoes (Williams and Meyer-Abich, 1955), fumaroles, and hot springs (Fig. 3). Many faults and contacts between different rock types channel the circulation of hydrothermal fluids surrounding the magmatic chambers of active as well as dormant volcanoes (e.g. López et al., 2004; Pérez et al., 2004). The most significant geothermal systems in El Salvador are aligned from west to east (Fig. 3): Ahuachapán and Chipilapa hydrothermal fields, Cerro Pacho and thermal springs on the shore of Coatepeque caldera lake, several bicarbonate springs at San Salvador volcano, possible sub-aqueous seeps in Ilopango caldera lake, the hydrothermal fields El Obraje and San Vicente associated with San Vicente volcano; Berlín geothermal field near Tecapa Volcano; the Chinameca hydrothermal field; and thermal springs at the shores of Olomega lake.

Geothermal energy has been exploited in El Salvador since 1975 at two sites: Ahuachapán and Berlín. There are some data on As in geothermal fields (e.g. Jasmin et al., 2005; Sullivan, 2008). Some of the data collected by industry have been made available to the public through ISOHIS (Isotope Hydrology Information System) as part of the Global Network of Isotopes in Precipitation (GNIP) formed by the International Atomic Energy Agency (IAEA).

3.3.1. Ahuachapán geothermal field

The Ahuachapán and Chipilapa geothermal fields are associated with the Concepción de Ataco caldera and the volcanoes Laguna Verde and Laguna de las Ninfas. The Ahuachapán andesites are recognized as the permeable unit comprising most of the reservoir (Electroconsult, 1984). The NNW–SSE striking faults present in the area are produced by the movement of the Caribbean Plate parallel to the Motagua–Polochic–Jocotán transverse fault that separates the Caribbean and North American plates (González Partida et al., 1997). This fault system is recognized as the main conduit for fluid transfer at the Ahuachapán geothermal field. Data for seven cold springs, one hot spring, one crater lake, and three domestic wells exist in the ISOHIS database (International Agency for Atomic Energy, IAEA). The waters discharged at Ahuachapán from cold springs have As concentrations from 0.01 to 0.09 mg L^{-1} (mean = 0.04 mg L^{-1}), with pH from 6.1 to 7.3 (mean = 6.7). Domestic well waters at Ahuachapán vary in As concentrations from 0.08 to 0.090 mg L^{-1} (mean = 0.08 mg L^{-1}), with pH from 6.6 to 7.5 (mean = 6.9). The waters of the crater lake have the highest concentration of As (0.21 mg L^{-1}) with a pH of 6.4 . Arsenic data for the geothermal wells under exploitation have not been published.

3.3.2. Coatepeque geothermal field

Coatepeque caldera forms part of the Santa Ana–Izalco–Coatepeque volcanic complex located in western El Salvador (Fig. 3). The caldera lies at the border of a hypothesized pull-apart structure that links two major segments of the El Salvador Fault Zone (ESFZ) (Agostini et al., 2006). This caldera formed as a result of volcano collapse 50 – 70 thousand years ago (Pullinger, 1998). Intracaldera activity has continued at Coatepeque, and the Cerro Pacho dome located to the southwest of the caldera, probably the most recently emplaced structure. Hydrothermal activity is visible at this dome as well as at hot springs discharging at the lake's shore in the same area. Arsenic data for hot springs and for lake waters are reported in McCutcheon (1998). For the hot springs, two values for As concentrations are reported: 3.1 and 1.5 mg L^{-1} . As ranges from 0.09 to 1.19 mg L^{-1} (mean 0.47 mg L^{-1} , $n = 7$) in the lake.

3.3.3. Ilopango Lake

Williams and Meyer-Abich (1955) stated that Ilopango caldera formed via three distinct collapse episodes that produced violent volcanic eruptions. The last caldera collapse generated the Tierra Blanca Joven deposit and occurred approximately 1600 years ago (A.D. 429) forming the basin that now contains the lake (Hart, 1981). Warmer water has been reported by fisherman in the southern area of the lake.

In Ilopango Lake, As concentration range from 0.15 to 0.78 mg L⁻¹ (mean = 0.53, n = 12) in the waters to 5.6 to 103.4 mg kg⁻¹ in the sediments (Ransom, 2002; López et al., 2009). For the sediments of Ilopango, statistically significant correlations were found for Li vs. As and for B vs. As (López et al., 2009), consistent with their common volcanic origin. However, the points of maximum concentrations in the sediments for As and B differ from those in the water (López et al., 2009). The areas with the highest concentrations of B and As in the water are located in the southern lake, corresponding to sediment samples with the lowest As and B concentrations. Previous investigations in soil gases in this caldera included samples along the perimeter of the lake (López et al., 2004). Comparison between these two studies showed that the southern part of the lake presents the highest emissions of carbon dioxide and concentrations of radon, following the general trend of the concentrations of As and B in the water (López et al., 2009), suggesting leaching from the sediments as one possible mechanism of As enrichment in the waters.

Ilopango Lake discharges into the Desague River, which is a tributary of Jiboa River. Arsenic data from these two rivers (Esquivel, 2007) showed a clear attenuation of As concentration with distance from the lake, suggesting sorption or co-precipitation processes that transfer the As from the water to the sediment or organic matter.

3.3.4. Berlín geothermal field

This The Berlín hydrothermal field is approximately 100 km east-southeast of San Salvador (Fig. 3) on in the northern flank of the basaltic-andesite Tecapa volcano. This geothermal field is located within NW-SE trending faults that form a 5 km-wide graben system that formed at the same time than the Berlín caldera collapse (100 Ka). Previous studies performed in the north-central area of the Berlín field suggest the presence of a groundwater system consisting of three principal aquifers (Shallow, Intermediate, and Deep) (Montalvo and Axelsson, 2000), with the deep aquifer as the geothermal reservoir. Data for springs and domestic wells in the Berlín area are listed and reported in the ISOHIS data base as well as other sources (e.g., Sullivan, 2008). However, only the springs with temperatures higher than around 33 °C contain As concentrations higher than 0.025 mg L⁻¹. The cold sources (n = 44, Sullivan, 2008) have concentrations of As ranging from 0.001 to 0.025 mg L⁻¹ (mean = 0.010 mg L⁻¹). For the hot springs, As concentrations range from 0.01 to 0.33 mg L⁻¹ (mean = 0.08 mg L⁻¹). Similarly, for the domestic wells, As concentrations are low, ranging from 0.004 to 0.042 mg L⁻¹ (mean = 0.020 mg L⁻¹, n = 16). Arsenic in the Na-Cl waters of the geothermal wells range from 7.8 to 16.7 mg L⁻¹ (mean = 11.7 mg L⁻¹) for five sampled wells (Jasmin et al., 2005). For these wells, pH ranged from 6.1 to 7.0 (mean = 6.4).

3.4. Nicaragua

Nicaragua has many geothermal fields and volcanoes, with the Momotombo geothermal field in exploitation since 1983. The geothermal resources identified in Nicaragua are (Fig. 3): Casita-San Cristobal, Cosigüina, El Hoyo-Monte Galán, El Najo-Santa Isabel, Isla de Ometepe, Managua-Chiltepe, Masaya-Granada-Nandaime, Momotombo, Nagrote-La Paz Centro, San Jacinto-El Tizate, and Tipitapa (Battocletti, 1999; Birkle and Bundschuh, 2007a). However, As data from these sites are limited.

3.4.1. Momotombo and Monte Galán geothermal fields

The Momotombo volcanic complex consists of several small volcanic cones and a caldera. Momotombo volcano is located on the eastern edge of the 4.5 km diameter Monte Galán caldera (Goldsmith, 1975). Two major fault systems are present in this area, the NW-SE fault system that forms the Puerto Momotombo Graben and the NE-SW fault system (e.g. the Puerto Sandino fault). These two fault systems are the preferential flow paths for hydrothermal waters. The westernmost, NE-SW trending fault seems to be the main conduit for the upwelling fluids of the caldera (Porrás et al., 2007).

In a comprehensive study of surface and groundwaters of the Managua area, Parello et al. (2008) report compositions of three spring samples collected between the Monte Galán Caldera and the Asososca de Leon volcano, close to the Momotombo volcano, as well as three samples from wells in the Momotombo geothermal field. The first three samples correspond to bicarbonate-rich waters with As ranging from 0.11 to 0.12 mg L⁻¹ (mean = 0.11 mg L⁻¹), and pH from 6.4 to 6.8. In comparison, the geothermal wells from Momotombo discharge Na-Cl waters that have As concentrations ranging from 1.7 to 2.7 mg L⁻¹ (mean = 2.1 mg L⁻¹), with pH from 8.1 to 8.4 (mean = 8.3).

3.4.2. Nicaraguan volcanoes

Arsenic has been determined in condensates from gases of several volcanoes in Nicaragua. For Cerro Negro, Momotombo, and Masaya volcanoes, Gemmel (1987) reports As concentration ranges of 0.03 to 0.10 mg L⁻¹ (mean = 0.07 for 7 samples), 0.23 to 0.49 mg L⁻¹ (mean = 0.30 for 5 samples with detectable As out of 8 samples), and 0.04 to 0.40 mg L⁻¹ (mean = 0.16 mg L⁻¹, for 3 samples), respectively, and 0.08 mg L⁻¹ at Telica volcano (one sample).

3.5. Costa Rica

Several geothermal resources have been identified in Costa Rica: Fortuna-Poco Sol Caldera, Irazú-Turrialba, Miravalles, Orosí-Cacao, Poás, Porvenir-Platanar, Rincón de la Vieja, and Tenorio (Battocletti, 1999). One of these areas, Miravalles, has 152 MW installed capacity in three different sectors of the volcano.

3.5.1. Rincón de la Vieja geothermal field

Rincón de la Vieja geothermal system is hosted in predominantly andesitic rocks. Springs in this system are characterized by low As concentrations with the exception of one area that discharges Na-Cl waters similar to the geothermal reservoir (springs Salitral Norte 1 and 2) (Birkle and Bundschuh, 2007b), with 10.6 and 10.9 mg L⁻¹ As concentrations, respectively (Hammarlund and Piñones, 2009). Arsenic concentrations in the geothermal reservoir range from 6.0 to 13.0 mg L⁻¹; with a mean equal to 9.9 mg L⁻¹ (n = 4). The other geothermal springs are conductively-heated meteoric waters (Birkle and Bundschuh, 2007b) with As concentrations ranging from 0.005 to 0.13 mg L⁻¹ (Hammarlund and Piñones, 2009; Hammarlund et al., 2009).

3.5.2. Miravalles geothermal field

This field in western Costa Rica is an andesitic reservoir with As concentrations ranging from 11.9 to 29.1 mg L⁻¹ (n = 13) with an average concentration of 24.4 mg L⁻¹ (Hammarlund and Piñones, 2009). Only one spring with acid pH (2.3) of Ca-SO₄-type shows high As concentrations of 4.56 mg L⁻¹, suggesting this water contains a magmatic component. Two Na-Cl-bicarbonate-type springs show high As concentrations (Na-Cl Salitral Bagaces 1 and 2) with 6 mg L⁻¹ of arsenic (Antonio Yock, pers. Commun.), and high Na and Cl concentrations of 2100 and 2600 mg L⁻¹, respectively (Birkle and Bundschuh, 2007b). These two springs should not be confused with the Na-HCO₃ spring Salitral Bagaces reported by Hammarlund and Piñones (2009) from the same site, which has low electrical conductivity and an As concentration of only 0.188 mg L⁻¹. This thermal spring (60 °C) has changed its characteristics from a permanent to an intermittent spring and sampling has become only occasionally possible. The other geothermal springs are likely generated by condensed steam or conductively-heated meteoric water which is reflected in their lower As concentration, ranging from 0.001 to 0.281 mg L⁻¹ (n = 10), with a mean of 0.112 mg L⁻¹ (Hammarlund and Piñones, 2009).

3.5.3. Costa Rican volcanoes

The concentration of As in gases emitted by several volcanoes in Costa Rica, as has been determined by several authors. The concentration of As in the gases of Poás volcano has been reported as 2.55 mg L⁻¹

(Signorelli, 1997), and 14.71 mg L^{-1} (Naranjo fumarole, Bundschuh et al. unpublished data). For Irazú, Rincón de la Vieja, and Hornillas Miravalles, Signorelli (1997) reports As concentrations for gas condensates as of 0.013, 0.050, and 0.050 mg L^{-1} , respectively.

4. North-Central and Northeastern Andean Regions of Ecuador

Ecuador has many volcanic centers and geothermal systems. Geothermal waters with high As concentrations are located in the north-central Andean region of Ecuador (Fig. 4) and the basin of Papallacta Lake in Quijos County (Fig. 5).

4.1. North-Central Region

This area is located between $1^{\circ}11' \text{ N}$ and $1^{\circ}30' \text{ S}$, and includes five provinces: El Carchi, Imbabura, Pichincha, Cotopaxi, and Tungurahua (Fig. 4). This region covers $30,134 \text{ km}^2$ and has a population of more than 3,600,000 inhabitants (Instituto Ecuatoriano de Estadística y Censo, 2001). The geology of this region is formed predominantly by andesitic to rhyolitic volcanic material (Baldock, 1983). For a complete chemistry of the different springs, see Cumbal et al. (2010).

4.1.1. El Carchi Province

In this province, Aguas Hediondas spring (P1 in Fig. 3) has a fairly high temperature (50°C) and a relatively low concentration of As (0.020 mg L^{-1}). The Aguas Negras springs (P5) As concentration is the lowest of the province (0.002 mg L^{-1}). In Rumichaca and La Calera springs (P8 and P12 in Fig. 3), the As concentrations are high compared with other thermal waters, reaching 0.403 mg L^{-1} and 0.684 mg L^{-1} , respectively. The average extractable As for the sediments at Aguas Hediondas spring (P1) increases downstream from 170.7 to 717.6 mg kg^{-1} . Two main factors contribute to the build-up of As in sediments: i) co-precipitation with calcite or calcium sulfate since the geothermal waters are oversaturated with respect to these minerals and ii) sorption on Fe(III) and Al(III) oxides and natural organic matter. Chemical analysis of sediment samples confirms

the presence of sulfur, iron, aluminum, and calcium. Thus, arsenic is retained within calcite and gypsum or is bound to large surface areas of oxyhydroxides or hydrated Fe(III) oxides (HFO) particles.

4.1.2. Imbabura Province

The Chachimbiro geothermal springs have As concentrations of up to 0.976 mg L^{-1} (0.876 mg L^{-1} on average). Environmental conditions contributing to elevated concentrations of As in Chachimbiro geothermal water include high bicarbonate concentration in the springs (bicarbonate = 216 mg L^{-1} in average), triggering the formation of soluble arsenite-carbonate complexes such as $\text{As}(\text{CO}_3)_2^-$, $\text{As}(\text{CO}_3)(\text{OH})^-$, and AsCO_3^+ that hinder sorption of As on sediments (Kim et al., 2000). These anions can compete with arsenates for sorption sites on metallic oxide surfaces thus keeping As in aqueous phase. Indeed, As content is not high in sediments of Chachimbiro springs (P17 and P16, 131.9 and 176.7 mg kg^{-1} , respectively) despite the high concentration in the waters.

4.1.3. Pichincha Province

Six geothermal water localities were analyzed for arsenic levels. Arauco springs show As concentrations below the detection limit of 0.002 mg L^{-1} (P22 in Fig. 3) and Cununyacu, La Merced de Nono, and Ilalo exhibit concentrations above 0.200 mg L^{-1} (P25, P28, P35). El Tingo (P33) and La Merced (P34) springs, which are also part of the Ilalo geothermal system, have As concentrations of 0.1 mg L^{-1} , and temperatures of 42.6 and 36°C , respectively. Analysis of sediments show highly extractable As at La Merced de Nono (P28: 329.7 mg kg^{-1}). High CO_2 concentrations at this site (640 mg L^{-1}) may prevent even greater build-up of As in sediments due to the formation of As-bicarbonate complexes (Sahai et al., 2007).

4.1.4. Cotopaxi Province

Results from the groundwater springs of Altamira farm show As concentrations in the range of 0.012 to 0.047 mg L^{-1} (P38, P39). In contrast, the concentration of As in sediments is relatively high (230 mg kg^{-1} in average). Additionally, organic matter content is

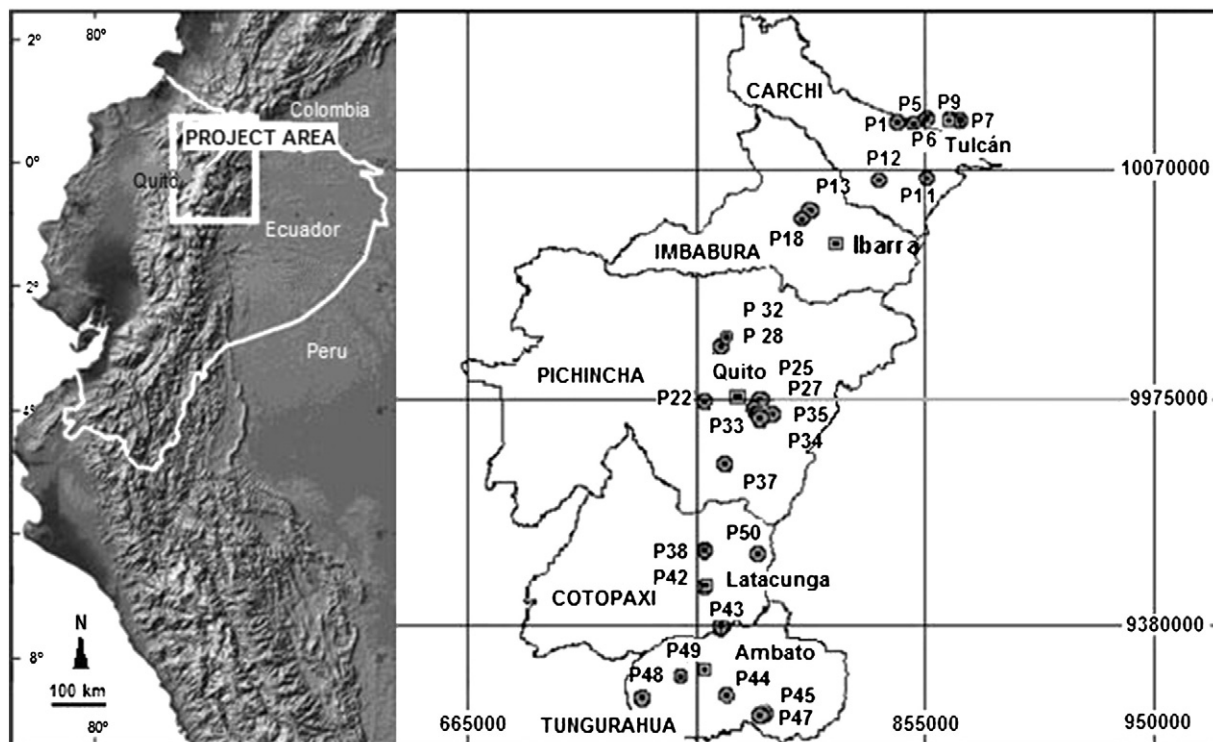


Fig. 4. Study area in the north-central Andean region of Ecuador and location of sampling sites. Modified from Cumbal et al. (2009).

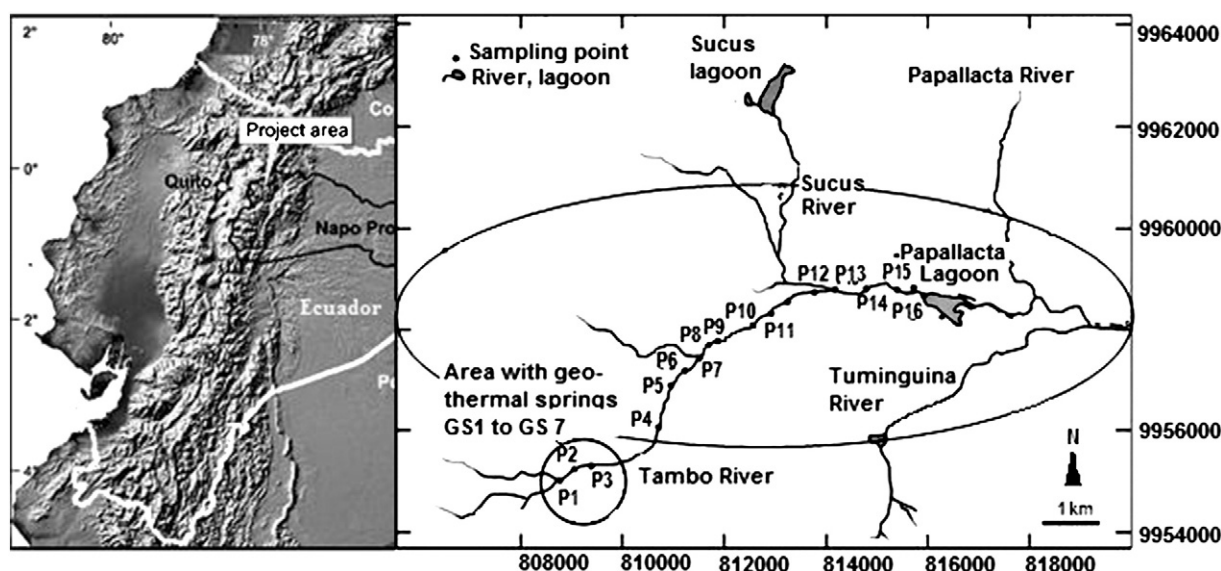


Fig. 5. Study area covering Papallacta and Sucus Lakes and the Tambo and Sucus Rivers. Sampling sites at the Tambo River are also shown (modified from Cumbal et al. (2009)).

around 29.5 wt.% in sediment samples, favoring the formation of As-organic matter associations in the sediments.

4.1.5. Tungurahua Province

High As concentrations are observed in the springs of Agua Santa (P45, As = 0.114 mg L⁻¹) and of El Salado (P47, As = 0.048 mg L⁻¹), located in the northern slopes of the Tungurahua volcano. Temperatures in these two springs are 54 and 48.9 °C, respectively. At Cunungyacu hot spring (P48), the As concentration is 0.047 mg L⁻¹ with a pH of 8.3 and temperature of 42.6 °C. Arsenic concentration in sediments of El Salado geothermal spring (P47) is 198.7 mg kg⁻¹. Ferric oxide concentration in sediments is 128 mg Fe g⁻¹ of sediment, with sorption onto the solid phase as the probable main mechanism of As accumulation.

4.2. Papallacta lake basin

Papallacta Lake is located in Quijos County, Napo Province, in the northeastern part of the country at an average altitude of 3360 m a.s.l. The lake formed as a result of a lava flow, known as Antisanilla, blocking a stream in 1760 (Bourdon et al., 2002), with water covering an average area of 330,000 m². The lake receives water from the Tambo River, some small cold streams, uncontrolled residual discharges from the Jamanco hot springs, and thermal groundwaters on the north side of the lake (Cumbal et al., 2009). Small thermal streams discharge into the Tambo River along approximately 12.8 km, impacting the water quality of the river and lake (see Fig. 5).

4.2.1. Arsenic in geothermal springs along the Tambo River

Arsenic levels in geothermal waters in the Papallacta basin are in the range of 1.090–7.852 mg L⁻¹. Speciation of As in two hot springs (GS1 and GS7 in Fig. 5) indicates the dominance of As(III) which amounts to 74.4 and 61.2% of total As concentration in highly reducing conditions. Total As concentrations for these springs are 3.152 and 6.120 mg L⁻¹, respectively. In addition, iron precipitates found in these geothermal springs are abundant, suggesting that the input waters are rich in Fe. Reductive dissolution of iron and manganese minerals, as observed in Bangladesh (Ahmed et al., 2004; Smedley and Kinniburgh, 2002) could be the main mechanism of As release during the uprising of reducing geothermal waters. Iron oxidation and precipitation of iron hydroxides occur as the geothermal waters reach the atmosphere. As(V) is predominant in springs GS3 (67.8%) and GS6 (66.5%), whose total As

concentrations are 3.555 and 7.852 mg L⁻¹, respectively. Temperatures of springs GS3 and GS6 are low (15.6 and 13.8 °C), probably the result of the mixing of spring waters with shallow groundwaters or oxygenated water recharge.

4.2.2. Arsenic in Papallacta Lake

Seven streams with water flows ranging from 0.3 to 4.5 L s⁻¹ (Tambo River – 220 to 1508 L s⁻¹) and unmeasured widespread thermal groundwaters discharge into Papallacta Lake. The highest As concentration comes from the Tambo River (0.149 mg L⁻¹) while all other streams exhibit concentrations in the range of 0.002 to 0.013 mg L⁻¹. Samples of water taken on the surface of the lake showed variations in As concentration from 0.22 to 1.74 mg L⁻¹ on April 22, 2006 and results from July 20, 2006 showed smaller values ranging from 0.086 to 1.43 mg L⁻¹. This variability in As concentration is mainly due to seasonal circulation patterns.

Sediment samples taken on the eastern and southeastern shores contain relatively high arsenic (540 and 613 mg kg⁻¹) in contrast to the lower sediment As levels on the northwestern and southwestern margins (60 and 72 mg kg⁻¹). This difference may be due to the continuous removal and re-distribution of sediments caused by the Tambo River input and also to As leaching from mineral and organic fractions of these sediments.

5. Bolivian Altiplano

Taquichiri et al. (2005) described the uses, location, and general chemistry of thermal springs in Bolivia, specifically the Bolivian Altiplano (BA), whose topographic elevation ranges from 3600 to 3900 m a.s.l. (PPO-3, 1996). The BA is an intra-mountain basin enclosed by the western and eastern chains of the Andes. Two systems presenting high As concentrations in the BA are considered here: the Poopo Lake basin and the salars of Coipasa and Uyuni.

5.1. Chemical Composition of the Poopo Lake basin Thermal springs

The Poopó Lake basin in the Oruro area is located in the central BA at an altitude of 3686 m a.s.l. Poopó Lake has an area that varies from 2650 km² to 4200 km² on a seasonal basis (Quintanilla, 1994). The thermal springs (Fig. 6) are commonly used for consumption, irrigation, and recreational purposes. The spring pH values range from 6.3 to 8.3 with

an average of 7.0 and temperatures range from 40 to 75 °C. Water samples indicate a diversity of water types: 50% are Na–Cl–bicarbonate, 43.7% are Na–Cl, and 6.2% are Na–bicarbonate (see Supplemental Table). Dissolved As concentration in the thermal springs ranges from 0.008 to 0.065 mg L⁻¹ and average 0.023 mg L⁻¹ (n = 16). The highest concentration of As is present in the Na–Cl water type (Ormachea et al., 2010). Arsenic speciation indicates that the predominant species is As(III) in nine samples and As(V) in five samples. Arsenic in the thermal springs could be attributed to the oxidation of sulfide minerals such as arsenopyrite and to the dissolution of volcanic rocks.

5.2. Salars of Coipasa and Uyuni

Surface water drainage were studied in the catchment areas of the salars of Coipasa and Uyuni located at the Bolivian Altiplano south-west of the Poopó Lake catchment area by Banks et al. (2004). Concentrations of As were up to 4600 mg L⁻¹ with a median of 0.034 mg L⁻¹ and were attributed not only to geothermal springs and fumarole sulfur deposits, but also to the oxidation of sulfidic minerals. Values of TDS increase from headwaters to downstream as a

consequence of evaporation processes and dissolution of evaporites. In comparison, concentrations of dissolved As decrease slightly downstream, probably as a consequence of adsorption on ferric oxyhydroxides of stream sediments.

6. Northern Chile

Two different systems with high As concentrations are considered from northern Chile: (1) the Camarones River area in the Arica and Parinacota regions (Fig. 7) and (2) the Tatío geothermal field.

6.1. Camarones River

The origin of As in the surface waters of the Arica and Parinacota regions (Fig. 7) is traced to the volcanic activity of the Andean Cordillera and As minerals contained in ignimbrites and other volcanic rocks as well as in sulfur calcretes (Mansilla and Cornejo, 2002). The Camarones River in this area has a high average concentration of As (1.0 mg L⁻¹) (Cornejo et al., 2006a, 2006b, 2008; Lara et al., 2006; Yañez et al., 2005), forming from the confluence of two tributaries, the Ajatama

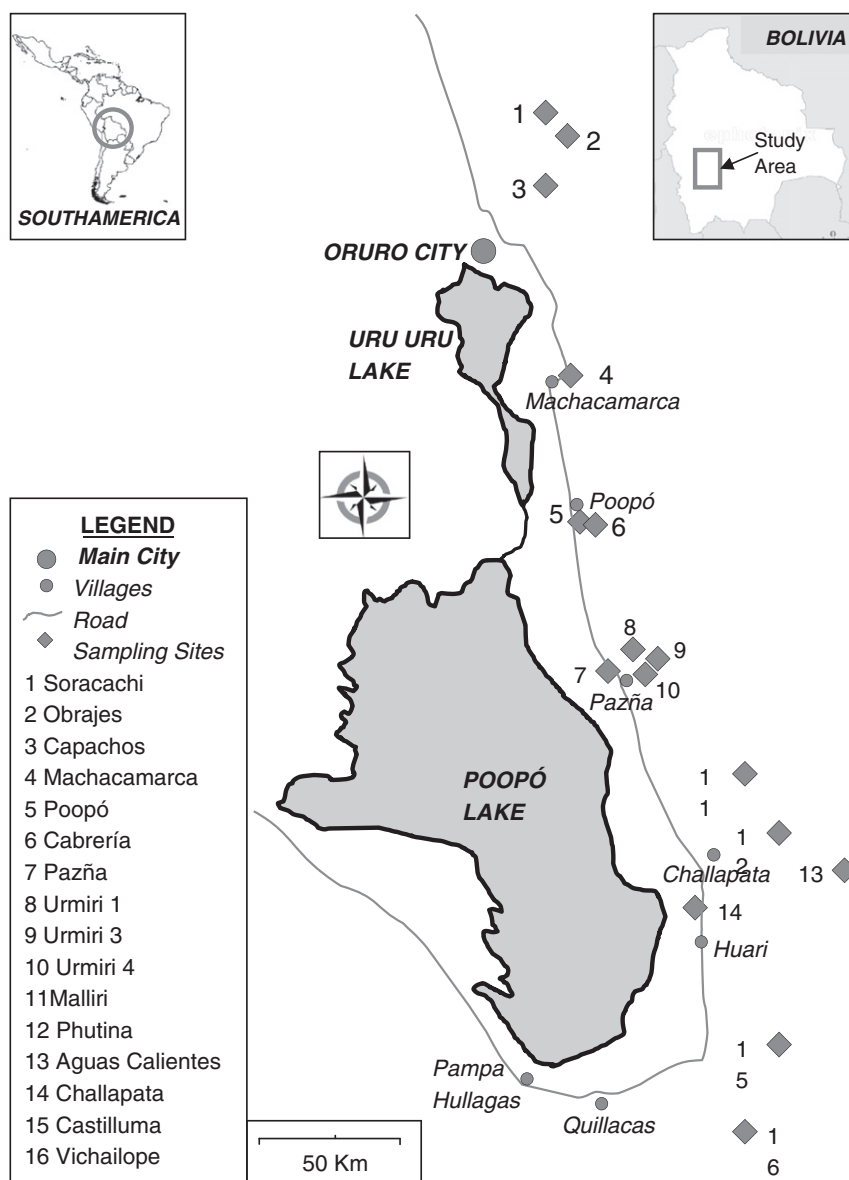


Fig. 6. Map of the BA showing the basins of Lake Titicaca, Desaguadero River, Uru Uru and Poopó lakes, and the Coipasa and Uyuni salars. Numbers indicate sampling stations for surface and groundwater monitoring. The study area and sampling sites of thermal springs are located southeast of the city of Oruro (modified from Quintanilla et al., 2009).

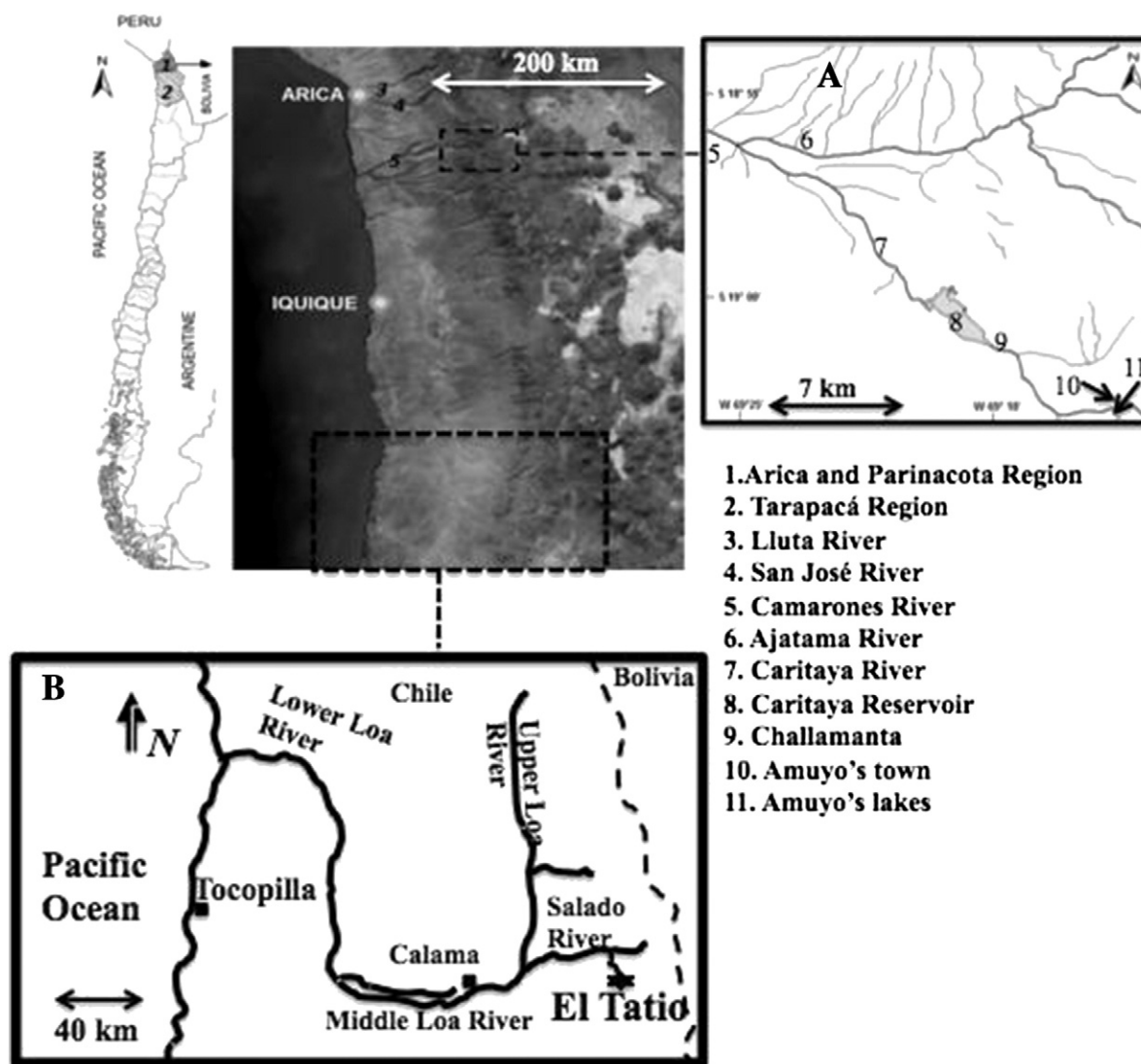


Fig. 7. Sites in northern Chile with high As concentrations from geothermal sources: A) Camarones River watershed and B) El Tatio geothermal field.

and Caritava Rivers (Fig. 7). The waters of the Ajatama River have low As concentrations (lower than 0.001 mg L^{-1}). In contrast, the Caritaya River has an As concentration of 2.35 mg L^{-1} (Fig. 7). The As enrichment of the Caritaya River is likely due to two different processes: inputs from three As-rich lakes and leaching of As-rich soils and rocks.

For the first process, high As concentrations are discharged into the river from the region of Amuyo Lakes (Fig. 7), which receive hydrothermal discharges at an elevation of 3700 m a.s.l., higher than the Caritaya River. Three lakes in the area have distinct colors that provide their identification: Red Lake (Wilacota), Green Lake, and Yellow Lake. The waters of these lakes contain the highest levels of As, B, and dissolved solids, with a mean As concentration of 11.0 mg L^{-1} .

For the second process, precipitation in the high Cordillera region is generally accompanied by electrical discharges from lightning that promote the formation of NO_x type gases responsible for acid precipitation (Mansilla and Cornejo, 2002). Infiltration of the acidic water and its reaction with As minerals increases the As concentration (Mansilla and Cornejo, 2002). This process explains the occurrence of rivers with high concentrations of As, such as the Camarones, Vitor, and Lluta Rivers in the transverse valleys of the region (Bundschuh et al., 2008). Arsenic concentration in these rivers decreases toward the ocean (Fig. 7). The presence of iron minerals in river sediments is probably producing sorption reactions that decrease the concentration of As in the oxidizing conditions that prevail along the river.

6.2. El Tatio geothermal system

El Tatio geothermal system is located in the Antofagasta region of northern Chile (Region II, Fig. 7) at an elevation of 4200 m a.s.l., and 100 km east of the town of Calama. It is the largest geothermal field in the southern hemisphere (Fernandez-Turiel et al., 2005), and a significant source of As and other typical geothermal elements such as F, Sb, Li, and B. Dozens of thermal springs, fumaroles, geysers, and boiling and mud pools occur in four main areas: Central, West, Corfo, and Geyser Blanco. The main hydrothermal reservoir is confined within the permeable Puripicar Formation and its Salado Member and recharge takes place about 15 km east of the field (Giggenbach, 1978; Tassi et al., 2010). The discharging water has a temperature of about 86°C and is of Na–Cl type. Arsenic concentration in the waters of one geyser is 7.6 mg L^{-1} , in two hot springs it is 27.0 and 30.1 mg L^{-1} , and in the Salado River it is 21.0 mg L^{-1} . Deuterium and oxygen isotopes from El Tatio waters show that they are the result of mixing between andesite-influenced water and meteoric precipitation (Tassi et al., 2010).

High dissolved silica concentrations at El Tatio result in a massive precipitation of siliceous sinter, mostly composed of amorphous silica, in discharge channels, (Fernandez-Turiel et al., 2005). The structure of the sinter depends on temperature and type of bacterial communities (Landrum et al., 2009). Arsenic is not incorporated into siliceous sinter and is quite mobile with almost constant As:Cl ratios several kilometers

downstream (Landrum et al., 2009). This is caused by extremely high aqueous silica concentrations that cover the surfaces of ferric oxyhydroxides with siliceous phases, inhibiting the adsorption of As, especially of As(III) (Swedlund and Webster, 1999). In contrast to As, Sb partitions into siliceous geyserite, probably co-precipitating as the nanoparticulate mineral cervantite during cooling (Landrum et al., 2009) and becoming quite immobile in comparison with As.

Discharge of geothermal arsenic in El Tatio geothermal field has a strong impact on the Rio Loa, which is used for the water supply of Antofagasta city (Romero et al., 2003). The As input occurs via the Salado River, which is a tributary of the Rio Loa, and the As is sourced from El Tatio geothermal waters. Arsenic concentrations in the river sediments are up to $11,000 \text{ mg kg}^{-1}$ close to El Tatio and remain around 700 mg kg^{-1} at the mouth of Rio Loa. Dissolved As concentrations in the Salado River decrease downstream due to dilution or sorption reactions, but they still are as high as 1.2 mg L^{-1} at the confluence with the upper Rio Loa.

7. Discussion

The presence of As in geothermal systems, mainly in geothermal waters and their impact on low-temperature aquifers, surface waters, and other surface environments are important in many geologic settings in Latin America. Geothermal As may degrade drinking water resources, as shown by the examples of Rio Loa (Chile), Papalacta Lake (Ecuador), and Ilopango and Coatepeque lakes (El Salvador).

Arsenic is leached from the host rocks of the geothermal reservoir, where high residence time, temperature and pressure, and reducing conditions (presence of As(III)), favor the release of As from rock minerals (Webster and Nordstrom, 2003). This leaching occurs along with other elements, such as Sb, B, F, Li, Hg, Se, Tl, and hydrogen sulfide (H_2S), making them good indicators of mixing of geothermal waters with low temperature aquifers or surface waters. Table 1 gives an overview of As concentrations, temperature, salinity, and pH in fluids of geothermal wells and geothermal springs in Latin America. A complete chemical data set is presented in the Supplemental Table. Generally, the highest As concentrations, typically from mg L^{-1} to tens of mg L^{-1} , are found in the fluids of geothermal reservoirs in volcanic rocks, and can be as high as 30.1 mg L^{-1} in El Tatio and 73.6 mg L^{-1} at Los Humeros, Mexico. Lower As concentrations are found in the hot springs of Guatemala, El Salvador, and Honduras, where As contents in fluids discharging from volcanic hydrothermal systems are as low as 0.010 mg L^{-1} , which can be explained by mixing with shallower groundwater, or lower residence time in the reservoir rocks. Compared with geothermal reservoirs hosted in volcanic rocks, much lower fluid As concentrations are found in geothermal reservoirs located in sedimentary rocks such as at Cerro Prieto (México) with a range of 0.25 to 1.5 mg L^{-1} (Birkle and Bundschuh, 2009; Birkle et al., 2010).

Geothermal waters change their chemical composition during their ascent from the geothermal reservoir to the ground surface due to several physical and chemical processes. Fluids, which ascend without loss of heat (or limited loss of heat due to conductive cooling), will emerge as Na–Cl waters with near neutral pH, high silica content, and a $\text{Cl}^-/\text{SO}_4^{2-}$ ratio > 1 . Fluids that correspond to this description are discharges from wells in geothermal fields under exploitation (e.g. Los Azufres in Mexico, Berlín in El Salvador, Zunil in Guatemala, see Table 1). These Na–Cl waters generally show the highest As concentrations of several mg/L . Rising geothermal waters, when mixed with near surface groundwater rich in bicarbonate become waters of bicarbonate type (e.g., Platanares PL-1, Honduras). Waters with a high content of H_2S gas, which condense near the ground surface, form pools of water with high SO_4^{2-} and low Cl^- concentrations (e.g., hot spring F-83 in Berlín geothermal field, El Salvador). Oxidation of H_2S in Na–Cl waters in the near surface environment gives rise to low pH and high SO_4^{2-} and Cl waters (e.g. Albergue Agroecológico hot spring, Rincón de la Vieja volcano, Costa Rica, see Supplemental Table). Oxidized sulfur forms

bisulfate ions (HSO_4^-), a reaction favored by decreasing temperature in the near-surface groundwater environment, producing low pH water. For the geothermal waters of Latin America, the distribution of all these types of waters are shown in the triangular plot for SO_4^{2-} , Cl^- , and alkalinity ($\text{HCO}_3^- + 2\text{CO}_3^{2-}$) of Fig. 8. The majority of the waters with As concentrations higher than 10 mg L^{-1} are Cl-rich waters, and a few of them have bicarbonate as the main anion. Only four of the high arsenic waters have concentrations of sulfate comparable to Cl and bicarbonate, three being lake waters from Amuyo Lake in northern Chile (Fig. 7). Relatively low concentrations of sulfate for As rich waters have been observed in other natural systems of the world, such as the glacial aquifers of central Illinois (Kelly et al., 2005) and in groundwaters from Bangladesh (Ravenscroft et al., 2001).

Precipitation of As due to bacterial reduction of sulfate has been proposed as a mechanism to explain low sulfate in high As waters (Rittle et al., 1995). Ravenscroft et al. (2001) suggested that the lack of correlation between As and sulfate in Bangladesh groundwaters indicated that As was not coming from the oxidation of arsenopyrite. This lack of correlation is also observed in geothermal waters from Latin America (Fig. 8). However, pyrite and arsenopyrite are common minerals in geothermal reservoir rocks. The lack of correlation is probably due to a reduction of the solubility of As minerals when sulfur is present promoting precipitation rather than dissolution of As minerals. Reducing conditions prevail along the pathways of ascending geothermal water until near the Earth's surface zone, where atmospheric O_2 becomes increasingly available, either during mixing of the geothermal water with cold water of oxidizing aquifers or when it discharges at the ground surface. At the surface, exposure to oxygen results in a fast oxidation of As(III) to As(V) and precipitation of different mineral phases (Alsina et al. 2007, Bundschuh et al., 2008), which removes As from the fluids to a variable extent. Although accumulated sediments at the bottom of evaporation ponds at the Los Azufres geothermal field (Mexico) are composed of more than 95% amorphous silica, the average abundance of 72.8 mg/kg for As confirms the precipitation potential of this element under oxidizing and/or cooling conditions (Birkle and Merkel, 2002).

Arsenic and Cl remain in the liquid phase during sub-surface boiling and phase separation (Webster and Nordstrom, 2003). Geothermal waters rich in Cl are usually also rich in As. However, Birkle et al. (2010) found a lack of significant correlation between As and Cl for the Mexican volcanic geothermal fluids. These authors postulate that As and Cl did not have the same origin, and suggested rock leaching as the major chemical process producing abundant As in Mexican volcanic geothermal fluids. This lack of statistically significant correlation is also observed in the data reported in the Supplemental Table for the different

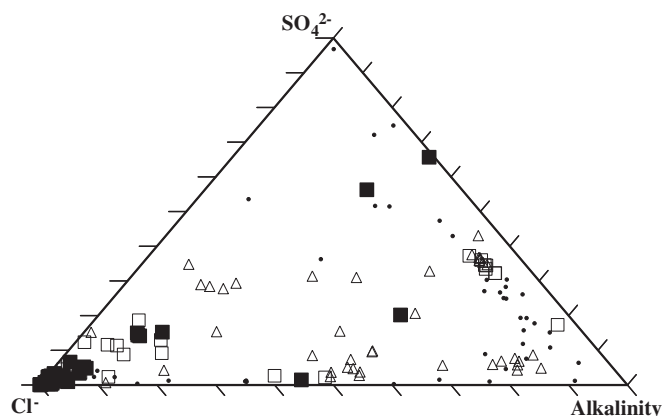


Fig. 8. Triangular diagram for SO_4^{2-} , Cl^- , and alkalinity of geothermal waters of Latin America. Concentrations of As are as follows: small circles = $\text{As} < 0.050 \text{ mg L}^{-1}$, small open triangles = $0.050 < \text{As} < 1.00 \text{ mg L}^{-1}$, open small squares = $1.00 < \text{As} < 10.0 \text{ mg L}^{-1}$, and large dark squares = $10.0 < \text{As} \text{ mg L}^{-1}$. Note high As concentrations for the waters that are rich in Cl.

geothermal sources of Latin America. Graphs showing the concentration of K vs. Na and Li vs. B from Supplemental Table data are in Figs. 9 and 10. In these figures, As concentration is shown in four ranges: $As < 0.050$, $0.050 < As < 1.0$, $1.0 < As < 10$, and $As > 10 \text{ mg L}^{-1}$. In Fig. 9, a positive linear trend of Na vs. K shows that geothermal waters with more than 10 mg L^{-1} of As have Na and K concentrations higher than 87 and 18 mg L^{-1} , respectively. In comparison, geothermal waters with less than 0.050 mg L^{-1} As have Na and K lower than 73 and 22 mg L^{-1} . Similarly, in Fig. 10, geothermal waters with $As > 10 \text{ mg L}^{-1}$ have B and Li higher than 26 and 6 mg L^{-1} , respectively, except in the wells of Los Humeros geothermal field in Mexico, where Li contents are lower than 1 mg L^{-1} even with As concentrations higher than 10 mg L^{-1} (see Supplemental Table). For these four ions, rock leaching is the dominant mechanism of their enrichment in water, suggesting that for As, this mechanism also dominates. Depleted Li values in Los Humeros fluids are likely due to reservoir rocks with low Li content. The enrichment of Cl in geothermal fields may come from host rock leaching, seawater intrusion, evaporation of seawater prior to infiltration, and/or gaseous HCl dissolution of magmatic components (Birkle et al., 2010).

Arsenic occurs predominantly in pyrite in volcanic rocks, or associated with Fe oxide in geothermally altered rocks (Ballantyne and Moore, 1988). Additionally, As-rich smectite (1500 to 4000 mg kg^{-1} As) has been found in geothermal precipitates in NW Japan (Pascua et al., 2005). As primary As minerals have not been documented for any of the described geothermal reservoirs in Latin America, abundant clay minerals in addition to sulfide minerals, could be a potential source for As dissolution during water–rock interaction under elevated temperature conditions ($> 280^\circ\text{C}$). The absence of primary As minerals is a common feature for global geothermal host rocks (Ballantyne and Moore, 1988). As postulated by Webster and Nordstrom (2003) for global geothermal water, neither magmatic fluids input, nor As mineralization, is a prerequisite for As enrichment in geothermal fluids.

The As dissolution process from host minerals is generally accelerated by elevated temperature conditions. Fluids from volcanic reservoirs (e.g., Los Azufres and Los Humeros from the TMVB, Las Tres Virgenes from a granodioritic basement, and the basaltic–andesitic reservoir of Berlin) show relatively constant As concentrations through varying temperature conditions, which indicates that temperatures above 230°C to 250°C provide optimal and stable conditions for As dissolution, in addition to high Cl concentrations (Birkle et al., 2010). In contrast, temperature conditions for sedimentary

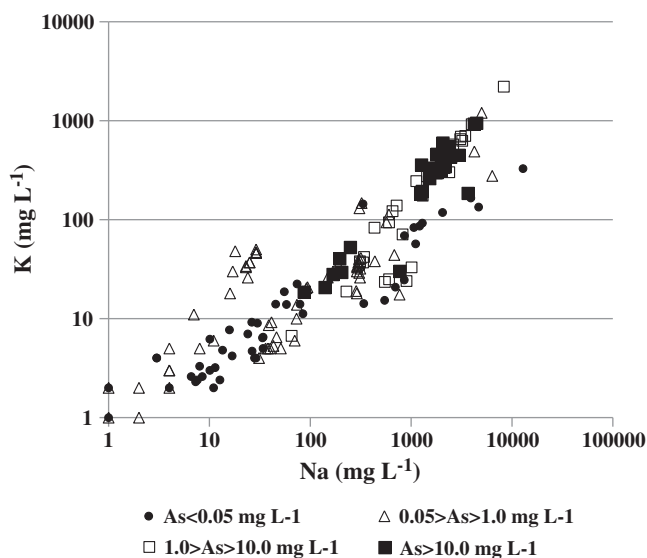


Fig. 9. K vs. Na concentrations in geothermal waters of Latin America. Arsenic concentrations in Fig. 7. Note high concentrations of Na and K in waters with high concentrations of arsenic.

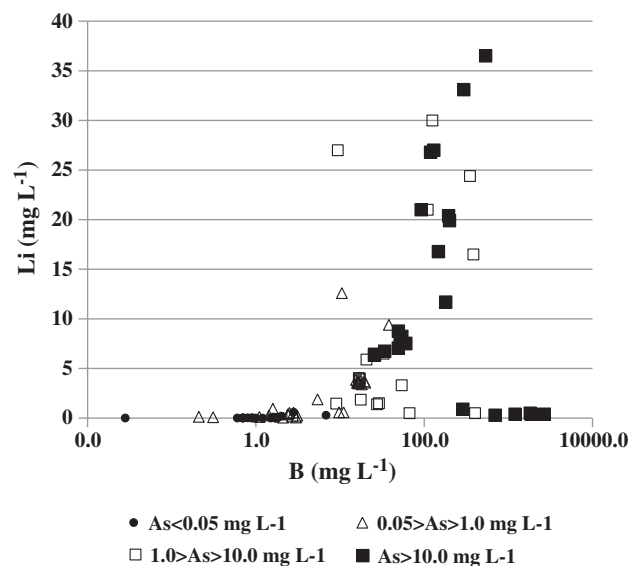
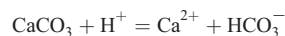


Fig. 10. Li vs. B concentrations in geothermal waters of Latin America. Arsenic concentrations in Fig. 7. Note high concentrations of B and Li in waters with high concentrations of arsenic.

reservoirs are not important for water–rock interaction processes, as suggested by low As concentrations for Cerro Prieto geothermal fluids (Birkle et al., 2010).

Volcanic gas condensates usually show As concentrations lower than 0.5 mg L^{-1} (e.g., Colima, Cerro Negro, Momotombo), consistent with their high sulfur species concentration. Data in Table 1 shows; waters influenced by active volcanoes have much lower As concentrations than those measured in recently exploited geothermal reservoirs. For example, at Colima volcano magnesium normalized enrichment factors and gas geochemistry (Taran et al., 2001) indicate As ascent from shallow degassing magma. At Popocatepetl, the presence of As in ash leachates and of tennantite that crystallized from magmatic volatiles in pumice samples (Larocque et al., 2008), provide evidence for its transport in gaseous emissions. However, concentration increases in the higher pH and most mineralized springs, indicating As release from the host rock, as well as possible concentration increase due to evaporation.

Calcium and magnesium concentrations in geothermal waters could also reflect the rock leaching process. However, Ca vs. Mg concentrations does not show a significant correlation. Carbonates, such as calcite, as well as clay minerals, are characteristic of geothermal mineral alteration (Giggenbach, 1988) and can buffer the composition of the solution. The dissolution of calcite is as follows:



with an equilibrium constant $K = \frac{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}}{a_{\text{H}^+}}$, enables $\text{Ca}^{2+}/\text{H}^+$ to be plotted vs. HCO_3^- concentration for the studied geothermal waters, as presented in Fig. 11. The bicarbonate concentration is calculated using pH and alkalinity values and the second dissociation constant for carbonic acid at the reported temperature. The equilibrium lines for calcite dissolution at 25°C and 100°C and the second dissociation constant for carbonic acid as a function of temperature were obtained using values reported in Shiraki and Brantley (1995). The majority of the data fall in a cluster around the 25°C and 100°C equilibrium lines suggesting that the solutions are close to or at equilibrium with calcium carbonate at the discharge temperatures.

Determination of As(III) has been reported only for three samples from Ecuador. However, the relatively low sulfate concentrations in comparison to bicarbonate and Cl (Fig. 8) suggest that As(III) is likely the dominant oxidation state for As in deep geothermal waters. When

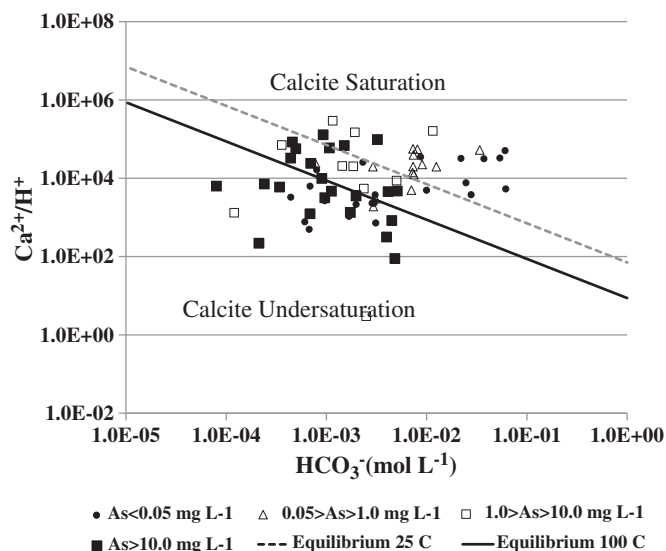


Fig. 11. $\text{Ca}^{2+}/\text{H}^{+}$ vs. HCO_3^- concentrations in geothermal waters of Latin America. Arsenic concentrations in Fig. 7. Data are clustered close to equilibrium conditions with respect to calcite.

reaching the ground surface, arsenite is quickly oxidized to As(V) (e.g., Papallacta basin in Ecuador). When geothermal water discharges into shallow aquifers, or surface waters, significant amounts of As will remain in solution, either as As(V) or as As(III). Arsenic species distribution depends on residence time of the groundwater in the aquifer and on the kinetics of As(III) oxidation.

A significant As content can be expected only in those geothermal waters which contain a significant component of geothermal reservoir water, which corresponds generally to Na–Cl waters. This is in contrast to shallow groundwater, which is heated by conduction or steam as observed in Rincón de La Vieja field, Costa Rica, where only two from 30 geothermal springs exhibited As concentrations of several mg L^{-1} , corresponding to those of the deep geothermal reservoir. Springs with elevated As concentrations (up to several $100 \mu\text{g L}^{-1}$) indicate that the spring water has a subordinate component of reservoir water, as shown for springs in El Zunil (Guatemala) and Berlín (El Salvador).

After the discharge of geothermal waters at the ground surface, several As attenuation processes take place in surface water bodies. Arsenic concentrations are diluted by mixing with As-free surface streams. Arsenic is also generally adsorbed on the surface of precipitated ferric oxyhydroxides. However, high concentrations of dissolved silica, which are common in discharging geothermal waters, may inhibit As adsorption due to saturation of the surface of ferric iron minerals as observed at the El Tatio site (Landrum et al., 2009). Furthermore, evaporative enrichment can maintain high As concentrations in waters in spite of As removal by adsorption on stream sediments. This has been observed in regions with arid and semi-arid climate such as the Rio Loa catchment in the Atacama Desert of Chile (Romero et al., 2003) and around the salars of Coipasa and Uyuni of the Andean Altiplano in Bolivia (Banks et al., 2004). Evaporation also increases pH and Cl concentrations and, thus, contributes to desorption and high mobility of As, which generally is present as oxyanionic species in surface streams (Banks et al., 2004; Sreck et al., 2004).

8. Conclusions

Data on As concentration in volcanic fluids and geothermal systems at several sites in Latin America suggest that there are two different sources of As in volcanic regions. One source is linked to volcanic gases emitted from volcanic craters after partitioning of As between the gas phase and the magma body, and the other is the As contained

in the erupted volcanic products that form the volcanic edifice. Leaching of As from the volcanic rocks occurs when groundwater with dissolved volcanic gases circulates throughout the volcanic edifice. Results for the As composition of volcanic gases are scarce and the data available give a very wide range of concentrations, from 0.050 to 1.2 mg L^{-1} for Mexican volcanoes, to 0.013 to 14.7 mg L^{-1} and 0.031 to 0.40 mg L^{-1} for Costa Rican and Nicaraguan volcanoes, respectively. The variability of the data even for a single volcano (e.g., see Póas Volcano above) can be explained by multiple factors. One is the difference in sampling and laboratory procedures that diverse researchers have used, and another is the state of activity of the volcano. In the same way that concentrations of carbon dioxide, sulfur dioxide, and other gases change with the state of activity of a volcano (e.g. Giggenbach, 1988; Todesco et al., 2004), it is probable that As concentrations also fluctuate. In addition, a clear understanding of the way of how As partitions between gas and liquid phases within a magmatic chamber is not possible yet. Further experimental, field, and theoretical research is needed to understand these partitioning processes at high temperatures.

Data for the geothermal systems presented in this paper as well as for other geothermal systems of the world (Planer-Friedrich et al., 2006) suggest that Na–Cl mature waters of volcanic systems present the highest As concentrations. Na–Cl waters typically have relatively low sulfate, high salinity, high Na and Cl concentrations, and a pH usually higher than 8. High As concentrations are commonly combined with elevated Li and B contents. Na–Cl waters are the result of a long-term water–rock interaction between groundwater enriched in volcanic gases and heated close to the magmatic chamber and the host rock that these waters encounter along their flow path (Giggenbach, 1988). They are usually discharged at the base or flanks of volcanoes and represent the main water source for many geothermal fields in exploitation.

As indicated by Birkle et al. (2010), the Na–Cl geothermal water is affected by ebullition during its ascent due to changes in hydrostatic pressure and by condensates at shallower levels forming waters that are low in As as observed in the surficial discharges of several geothermal systems in Latin America (e.g., Los Hornos geothermal field, Berlín geothermal field). Mixing of Na–Cl geothermal waters with shallower meteoric waters can produce bicarbonate-rich waters with low to intermediate As concentrations (e.g., Momotombo geothermal field).

Data for the studied sites in Ecuador, Northern Chile, and Ilopango Lake indicate that the fate of As after water discharge from thermal springs depends on the chemical composition of the water and sediments (e.g., presence of ferric iron minerals able to sorb the As) and the concentration of organic matter. Oxidation of As(III) to As(V) occurs as the waters come into contact with the atmosphere. The oxidation process seems to be catalyzed in the presence of organic matter by bacteria attached to macrophytes (Wilkie and Hering, 1998). The presence of bicarbonate, chloride, and silica in solution seems to inhibit the sorption process of As by iron minerals, as observed at La Merced de Nono in Ecuador. Immobilization of As by sorption onto iron minerals in surface waters is an important natural remediation process for As contamination. The data reported in this paper (different provinces in Ecuador, Camarones River in Chile, outlet river from Ilopango Lake in El Salvador) suggest that natural remediation of As contamination is occurring, and explains why As contamination is more important in groundwaters than in surface waters. For the case of caldera lakes rich in As (as in Coat-epeque and Ilopango lakes of El Salvador) or for other lakes such as Papallacta and Amuyo Lakes in Ecuador and Chile, respectively, the water/sediment ratio is high and does not allow for natural attenuation. Significant transfer of As from water to sediments can occur when water circulates along rivers where the water/sediment ratio is lower than in lakes and conditions are more oxygenated, favoring sorption processes in iron minerals. Other processes such as evaporation can cause increases in pH and can maintain high As concentrations in waters in spite of As removal by sorption on stream sediments, as observed in arid and semi-arid climate regions (e.g., Camarones River).

More research on As in volcanic and geothermal systems is needed for a better understanding of the processes that determine the concentration of As in groundwater, volcanic gases, and surface waters. More extensive monitoring of the water quality and health of the inhabitants of the Latin American Pacific Rim is crucial for ameliorating the effects of arsenic in waters.

Supplementary material related to this article can be found online at doi:10.1016/j.scitotenv.2011.08.043.

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